Proceedings of the International Symposium on Enhanced Landfill Mining

Towards zero-waste valorisation of landfilled stocks and fresh flows of critical-metal-containing industrial process residues: a critical review

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Abstract

Unlike China, Russia or South-Africa, Europe is not gifted with large, easily accessible, rich ore deposits containing valuable metals. However, Europe does have large quantities of secondary industrial residues. These residues constitute both *flows* of freshly produced and *stocks* of discarded materials. The latter category refers to the residues which have been deposited in so-called mono-landfills (incl. tailing ponds) throughout Europe, during the course of the last 100-150 years. Although the classical definition of Enhanced Landfill Mining (ELFM) – "*the integrated valorisation of landfilled waste streams as materials and energy, using innovative transformation and upcycling technologies, and respecting the most stringent social and ecological criteria*" – was mainly developed for landfills rich in Urban Solid Waste, it can also be adapted to the mining of these mono-landfills. Hence, Enhanced Landfill Mining of critical-metal-containing industrial mono-landfills implies the zero-waste valorisation of these materials, resulting in the recovery of the critical (and base) metals and the valorisation of the residual mineral matrices. In terms of accessibility, volumes and metal concentrations, some of the most interesting industrial process residues are considered to be: (1) bauxite residue; (2) phosphogypsum; (3) iron-rich sludges; (4) metallurgical slags; and (5) bottom ashes and fly ashes. This review gives an overview of the potential of these residues for recovery of critical elements and the state-of-the-art of the recovery technologies. In the concluding section the importance of the zero-waste valorisation concept is highlighted.

Introduction

Europe is confronted with a number of challenges along the entire raw materials supply chain. The European Commission has identified a series of 20 critical raw materials, for which there exist a large supply risk in Europe.[1] This list includes the heavy and light rare earths, platinum-group elements, gallium, indium, cobalt, germanium and antimony. To secure a diversified and sustainable access to critical raw materials, Europe needs to unleash the potential of its own resources. This has been explicitly prioritised in the recently published Action Plan for the Circular Economy by the European Commission (COM(2015)614/2).[2] However, unlike China, Russia, Australia or South Africa, the European continent is not gifted with large, easily accessible ore deposits rich in critical metals. If available at all, EU ore deposits are typically present in extreme environments or at greater depths, making their exploitation a risky business both economically and environmentally. As highlighted in the final report of the European Rare Earth Competency Network (ERECON), the rare-earth 2010-2011 supply crunch should act as a wake-up call to businesses and governments, highlighting the fact that critical metals should not be taken for granted.[3] In the case of the rare-earth crisis, Europe could only develop a *re-active strategy*, which consisted, amongst other, to invest in research and development, in projects related to (1) primary mining of EU rare-earth deposits (for instance the Norra Kärr deposit in Sweden and the Kvanefjeld deposit in Greenland), (2) substitution of critical rare earths by less critical rare earths or even other metals, and (3) recycling of End-of-Life products (e.g. NdFeB magnets or Eu/Y rich compact fluorescent lamps). It was hoped for that this combination would lead to a more diversified and sustainable rare-earth supply chain. Paradoxically, with rare-earth prices decreasing since the mid-2011 peak price, many of the developed recycling processes or EU rare-earth mining projects are currently uneconomic. Nevertheless, quoting the ERECON report, "*a repeat of the 2010/11 supply crisis remains a distinct possibility*", as competitive, reliable and sustainable access to rare earths is still far from secured.[3]

It is vital that Europe draws lessons from the rare-earth crisis. In the case of critical metals other than the rare earths, a supply crunch has not yet actually occurred. This implies that there is time to develop *pro-active solutions*, thereby avoiding the supply problems that occurred for the rare earths and which led to some EU manufacturers of next generation cleantech products flying supplies from one plant to another to avoid production outages. Hence, there is an urgent need to generate eco-friendly and cost-effective technology that is capable to extract critical metals from a diversity of European feedstocks.

Enhanced Landfill Mining of industrial mono-landfills

A very interesting and widely available feedstock is constituted by secondary industrial process residues. Europe has an extremely rich industrial ecosystem of interconnected ferrous and non-ferrous (copper, zinc, aluminium, lead etc.) metallurgical companies (focus of Figure 1), thermal treatment facilities and companies processing phosphate rock. Combined, the involved industries generate vast amounts of easily accessible industrial process residues, including a wide variety of tailings, slags, sludges, drossess, ashes and dusts. These residues constitute both *flows* of freshly produced residues and stocks of materials, which have been deposited in so-called mono-landfills (incl. tailing ponds) during the course of the last 100–150 years. Mono-landfills, i.e. landfills with one, relatively homogeneous industrial waste stream, are typically privately owned by the company producing the industrial residue. Access to these typically large and homogeneous landfills is, hence, more straightforward than is the case with the Urban Solid Waste (USW) landfills (see Figure 2: infographic developed by EURELCO).[4] Although the USW-based landfills are far more numerous than the industrial mono-landfills, they – generally speaking – present more practical barriers, as they are (1) (in most cases) publicly owned, (2) smaller in volume and size, (3) more heterogeneous in content, and (4) located in the direct vicinity of cities or smaller villages, inhibiting landfill mining activities. Although the classical definition of Enhanced Landfill Mining (ELFM) – "*the integrated valorisation of landfilled waste streams as materials and energy, using innovative transformation and upcycling technologies, and respecting the most stringent social and ecological criteria*"[5] – was mainly developed for USW-based landfills, it can also be adapted to the mining of these mono-landfills. Hence, Enhanced Landfill Mining of critical-metal-containing industrial mono-landfills refers to the (near)-zero-waste valorisation of landfilled industrial process residues, resulting in both the recovery of the critical (and base) metals and the valorisation of the residual mineral matrices into engineered products, which can partially replace fossil-fuel intensive products such as Portland cement.[6] This review gives an overview of the critical metal potential for a selected group of industrial process residues that have been and are still being stockpiled in mono-landfills, being: (1) bauxite residue from the aluminium industry; (2) phosphogypsum from the phosphate industry; (3) iron-rich sludges (e.g. goethite and jarosite) from the zinc industry; (4) metallurgical slags; and (5) bottom ashes and fly ashes from incineration plants. In the concluding section, key attention is given to the zero-waste valorisation character of the proposed flow sheets, which are relevant for both the (landfilled) *stocks* and (fresh) *flows* of these residues.

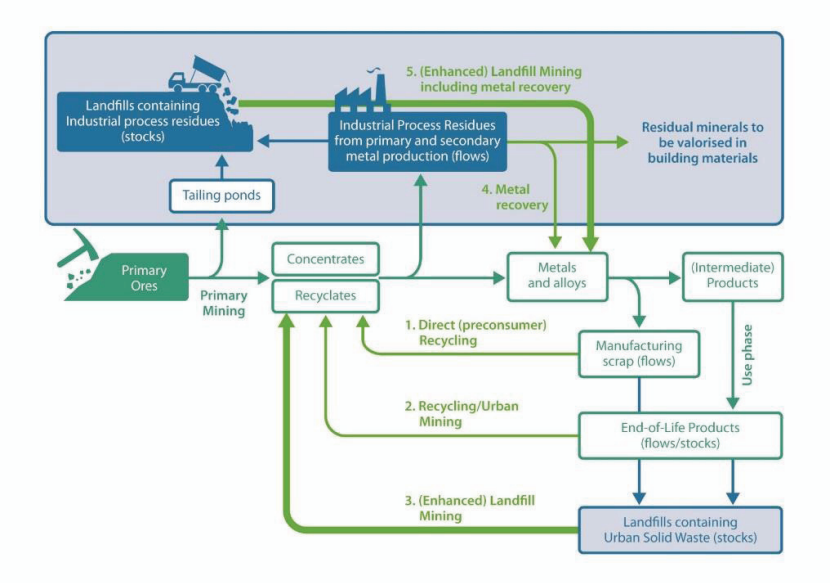

Figure 1: Closing the loop through technospheric mining, showing the importance of metal recovery from both the flows and stocks of industrial-process residues from primary and secondary metal production

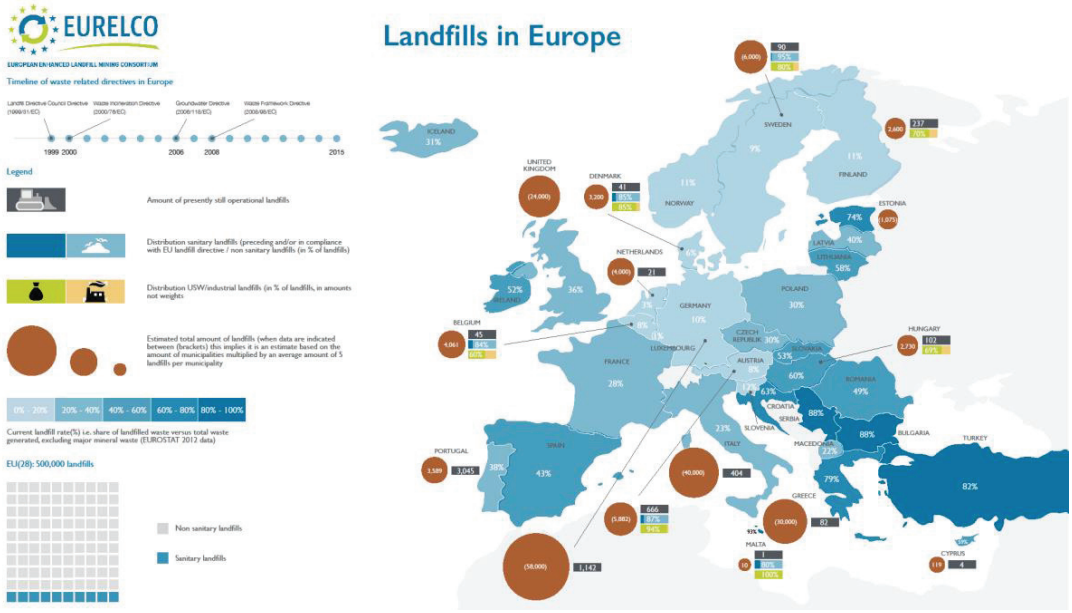

Figure 2: In 2015 EURELCO launched a bottom-up inventory exercise to obtain better data on Europe's landfills. Data were obtained for 15 EU Member States, with respect to current landfill rates, the amount of still operational landfills, the total amount of landfills and the distribution ratios sanitary vs. non-sanitary landfills and MSW vs. industrial landfills.[4] The

inventory show that at least 90% of Europe's landfills are "non-sanitary" landfills, which predate the EU's Landfill Directive (1999), and that the majority of landfills are MSW-based landfills. Nevertheless, depending on the Member State, between 0 and 40% of the landfills contain predominantly industrial waste, incl. the mono-landfills addressed in the present paper.

Bauxite residue (red mud)

Bauxite is the most important aluminium ore and it is a mixture of impure hydrated aluminium oxides. Depending of the type of deposit, gibbsite, boehmite or diaspore is the principal aluminium component. Bauxite contains only between 30–50% alumina, Al_2O_3, the rest being silica, various iron oxides, titanium dioxide, but also calcium, sodium and small amounts of zinc, gallium, nickel, vanadium, zirconium, niobium, thorium, uranium and rare earths.[7,8] The alumina must be purified before it can be refined to aluminium metal. This is done using the Bayer process, where bauxite is digested in a hot sodium hydroxide solution. This converts the alumina to aluminium hydroxide, which dissolves in the hydroxide liquor. The other components of bauxite do not dissolve. The solution is clarified by filtering off the solid impurities, which forms the so-called *bauxite residue* or red mud. The actual composition of bauxite residue depends on the type of bauxite, the mining location and the process parameters of the Bayer process. The pH of the wet red mud slurry is about 12. With a worldwide annual production of 120 millions of tonnes and a total inventory of 2.7 billion of tonnes, stored in huge holding ponds (Figure 3), bauxite residue poses a significant and hazardous problem. The latter was revealed recently by the dam failure of the Ajka refinery in Hungary and the resulting loss of human lives and environmental catastrophe. In Europe, besides Hungary, refineries exist in Bosnia Herzegovina, France, Germany, Greece, Ireland, Italy, Romania, Slovakia and Spain. Unlike other high volume wastes (fly ash, metallurgical slag), bauxite residue finds no industrial application besides minor use in cement and ceramic production. Many researchers have already looked at the valorisation of bauxite residue, besides its use in the construction industry. Bauxite residue has a high metal content and extraction of metals from bauxite residue can be economically feasible.

Figure 3: Bauxite residue (red mud) holding pond, in the vicinity of Stade, Germany. Copyright: Ra Boe / Wikipedia.

Iron is a main constituent of bauxite residue, and it can make up to 60% of the mass of the bauxite residue. In fact, its red colour is caused by the oxidised iron (mostly hematite or Fe_2O_3). In view of the rather large content of iron oxide, attempts have been made in the past to use bauxite residue as a source of iron. Iron recovery studies were initiated as early as in the 1950s and may be classified into two major approaches, i.e. smelting and solid state reduction. In the former, bauxite residue is treated in a blast furnace in the presence of a reducing agent where the iron oxides are reduced, generating pig iron and a titanium-rich slag (also containing the REE).[9,10] In the solid-state reduction the bauxite residue is mixed with a reducing agent or contacted with a reducing gas at certain temperature, resulting in the formation of metallic iron or the conversion of ferric iron to magnetite, which could either be used for steelmaking or as a charge to the blast furnace.[11] So far, these iron recovery processes have not been commercially successful, because of specific problems associated with bauxite residue. The large sodium content of bauxite residue prohibits the use of blast furnaces where the high temperatures lead to the evaporation of sodium oxide in the lower (hotter) regions of the blast furnace and its re-deposition in the colder regions, where it attacks the ceramic refractory bricks and also leads to the formation of so-called *sodium nests*, which are hard outgrowths that obstruct the free flow of the charge inside the furnace. Moreover, bauxite residue contains a significant amount of water, which would have to be removed first, thus representing a high cost if fossil fuels are used for drying.

Besides the recovery of iron from bauxite residue, researchers have tried to recover other elements as well: aluminium, titanium, gallium, vanadium and especially the rare

earths.[6,12-14] During the processing of bauxite by the Bayer process, all the rare earths end up in the bauxite residue. The enrichment factor of the rare earths in bauxite residue compared to bauxite is about a factor of two. The average concentration of rare earths in bauxite from Greece is 506 ppm, whereas the average concentration of the resulting bauxite residue is 1040 ppm.[15] Bauxite residue is rich in scandium.[6,16] Bauxite residue from Greece contains about 130 ppm, whereas bauxite residue produced from Jamaican bauxite has a scandium concentration of up to 390 ppm. However, the bauxite residue produced from bauxites from Moengo in Suriname have the highest rare-earth concentrations, with scandium concentrations as high as 1700 ppm. These scandium concentrations are much higher than the average abundance of 22 ppm of scandium in the Earth's crust, and point to a significant enrichment of scandium in bauxite and in bauxite residue. There exist minerals with a high scandium content (e.g. thortveitite and lolbeckite), but they form only very small deposits. The lack of rich scandium deposits hampers the widespread use of scandium, although scandium could find useful applications as an alloying metal for aluminium and as a recyclable Lewis acid catalyst for the production of fine chemicals. For these reasons, the recovery of scandium from bauxite residue could be of high economic interest. Scandium represents over 95% of the economic value of rare earths in bauxite residue.

There are numerous studies on the extraction of rare earths, and of scandium in particular, from bauxite residue.[6,12-14] The two main approaches are either purely hydrometallurgical processes or a combination of pyrometallurgical and hydrometallurgical processes. The purpose of the hydrometallurgical processes is to selectively leach the minor metals from the bauxite residue, leaving behind the major components such as iron oxides.[17,18] It has been an important discovery that the rare earths are readily leachable from bauxite residue by diluted mineral acids, whereas these elements cannot be leached from bauxite under the same experimental conditions. After leaching, the rare earths can be recovered from the leachate by selective precipitation as the oxalate, or by solvent extraction. The rare earths can be selectively dissolved by digesting bauxite residue with a dilute acid solution made by dissolving SO_2 in water (sulphurous acid), leaving most of the iron undissolved.[19] Also sodium, aluminium and silicon present under the form of sodalite are brought into solution, but the rare earths can be recovered by solvent extraction. A comparative study of leaching with different acids (HCl, HNO_3 or H_2SO_4, H_2SO_3), has shown that 0.5 M HNO_3 is the best leachant and that the leaching can be performed at ambient temperatures and pressures.[17] 80% of the scandium present and 96% of the yttrium could be recovered, but the leaching procedure was less efficient for the light lanthanides (30 to 50% recovery). Chenna have performed an in-depth study of the leaching of rare earths from red mud with different acids (HCl, HNO_3, H_2SO_4, CH_3COOH, CH_3SO_3H and citric acid).[18] The recoveries yields for rare earths were similar in all acids at low acid concentrations (<1 N), except for citric and acetic acid, which yielded lower recoveries. Initially, acid was consumed for the neutralization of the alkali and

aluminosilicates. Extraction of the rare earths was the highest for HCl leaching compared to other acids, but the iron leaching was also high. About 70 to 80% of the rare earths could be recovered from the bauxite residue using 6 N HCl leaching for 24 h duration at temperature of 25 °C. The leaching data show that scandium in bauxite residue is very closely associated with iron. Most combined pyro/hydrometallurgical treatments of bauxite residue use a pyrometallurgical step to first recover iron from bauxite residue and to subsequently concentrate the rare earths in an oxide slag.[10] The approach to extract iron from bauxite have been described above. The hydrometallurgical step consists of leaching the rare earths from the slag with a diluted mineral acid.

Ochsenkühn-Petropoulou and co-workers developed a pilot-scale setup for recovery of rare earths from bauxite residue, which as optimised for the recovery of scandium (Figure 4).[20] This process includes acid leaching of the bauxite residue with a dilute HNO_3 solution, separation of scandium, yttrium and the lanthanides from the co-leached main elements such as iron by ion-exchange resins, and subsequent treatment of the eluate by solvent extraction for further purification and enrichment of scandium. In the Canadian Orbite process, bauxite residue is leached with a concentrated HCl solution in an autoclave at temperatures between 125 and 150 °C (Figure 5).[21] This brings aluminium, iron and the rare earths into solution. By saturating the leachate with HCl, it is possible to induce crystallisation of $AlCl_3 \cdot 6H_2O$. Solid $AlCl_3 \cdot 6H_2O$ is separated from the solution and converted by calcinations to Al_2O_3, with recovery of HCl gas. The remaining solution is concentrated and $FeCl_3$ is hydrolysed to Fe_2O_3 (hematite) between 155 to 170 °C. After removal of Fe_2O_3 a solution of rare earths is obtained, from which the rare earths can be recovered by solvent extraction.

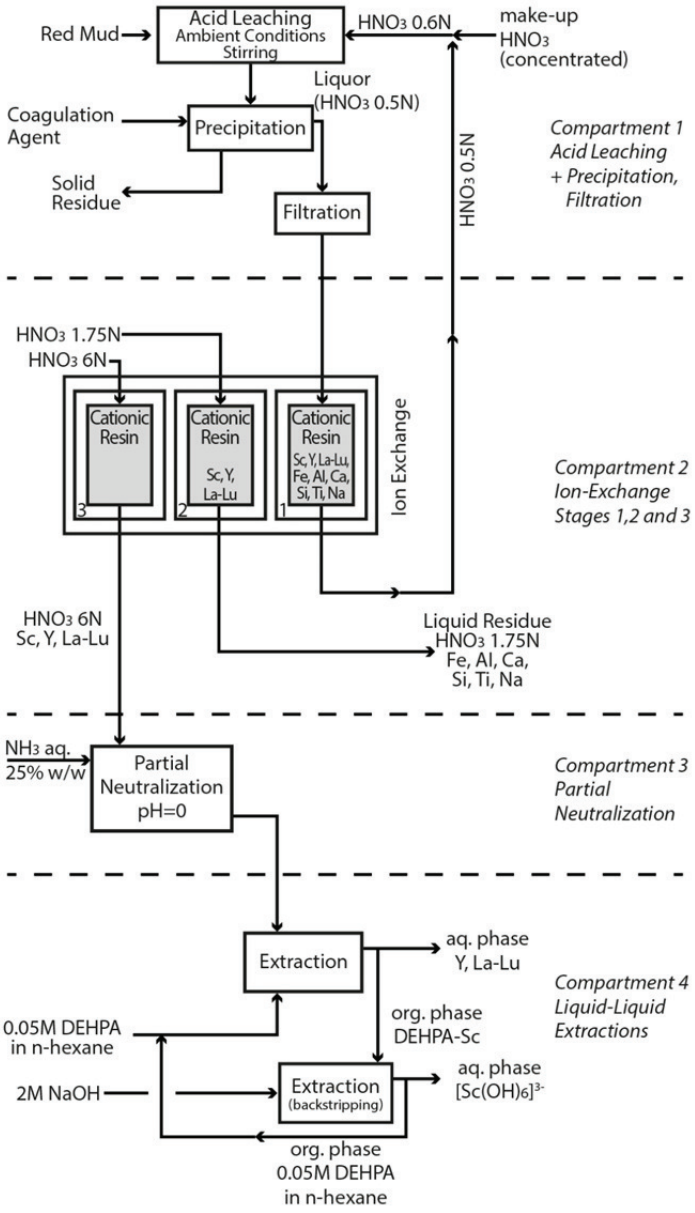

Figure 4: Conceptual flow sheet for the recovery of scandium from bauxite residue by a HNO_3 leaching method. Adapted from Ref. 20. Copyright American Chemical Society

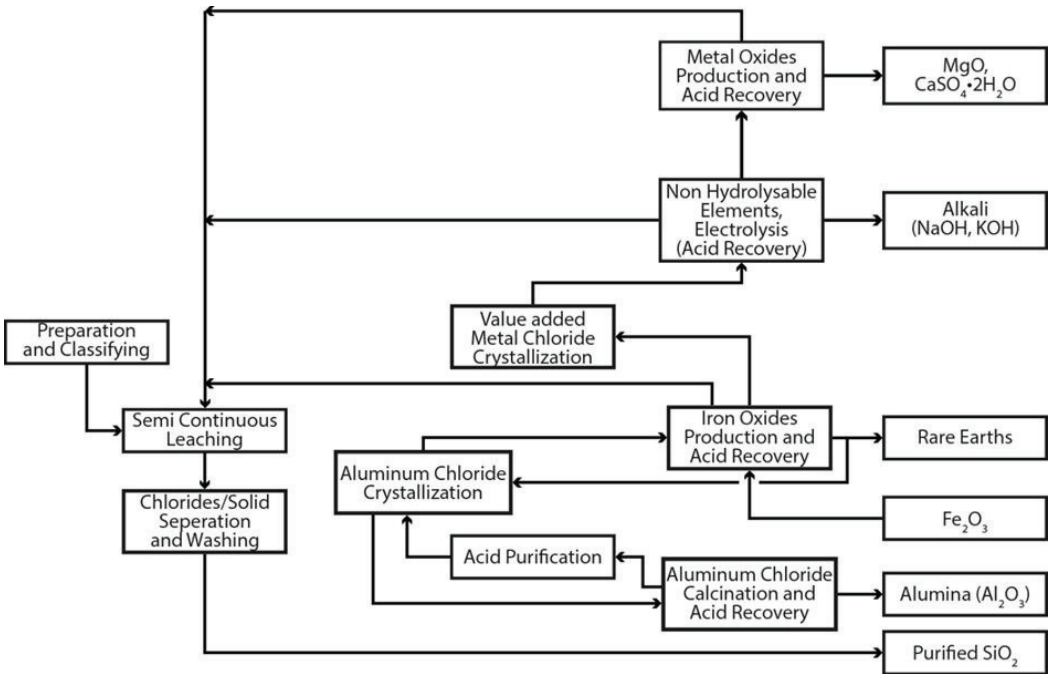

Figure 5: Flow sheet of the Canadian Orbite process for zero-waste valorisation of bauxite residue, including recovery of rare earths. Adapted from Ref. 21

Phosphogypsum

Phosphogypsum is the main by-product of the production of phosphoric acid and it is formed by the acidic digestion of phosphate rock.[22] The main mineralogical component of phosphate rock (also known as phosphorite) is apatite, $Ca_5(PO_4)_3(OH,F,Cl)$. The digestion is mainly done by sulphuric acid, although also nitric acid can be used. Depending on the production method, the phosphogypsum formed consists primarily of either calcium sulphate dihydrate, $CaSO_4 \cdot 2H_2O$ (gypsum) or calcium sulphate hemihydrate, $CaSO_4 \cdot \frac{1}{2}H_2O$, and with small amounts of silica, fluoride and unreacted phosphate rock. The amount of phosphogypsum produced during phosphoric acid production exceeds the mass of the product, i.e. 4.5 to 5.5 tonnes of phosphogypsum are generated per tonne of P_2O_5.[23] The phosphogypsum residue is landfilled or stored in waste stacks (Figure 6). The phosphogypsum stored in waste stacks consists in general of calcium sulphate dihydrate. It contains also trace amounts of many other elements, including thorium, uranium and rare earths, which were originally present in the phosphate rock. The concentration of rare earths in phosphate rock is in general only between 0.01 and 0.1 wt%, although phosphate rock of the Kola peninsula in Russia can contain up to 1.0 wt% of rare earths.[24-26] Cerium, lanthanum

and neodymium compose about 80% of the total rare-earth content. The rare earths are concentrated in phosphogypsum during the production of phosphoric acid. About 70 to 85% of the rare earths originally present in the phosphate rock end up in the phosphogypsum. The rest remains dissolved in the leaching solution, which also contains the phosphoric acid. Less rare earths are incorporated in the phosphogypsum if the leaching is performed at lower temperatures or with less concentrated sulphuric acid. The average concentration of rare earths in phosphogypsum is 0.4 wt%.[24] This seems to be a very low concentration in comparison with other rare-earth ores. The rare-earth deposits that are currently mined have a rare-earth oxide (REO) content between 3 and 15%. However, given the enormous amounts of phosphate rock processed every year and the fact that rare earths are just a by-product of the phosphoric acid production, phosphogypsum presents a valuable source of rare earths. The potential of phosphogypsum as a source of rare earths has already been recognised in the 1960s. In comparison with bauxite residue, phosphogypsum contains lower concentrations of scandium.

Figure 6: Phosphogypsum stack located near Fort Meade, Florida (USA). Copyright: Harvey Henkelmann /Wikipedia

About half of the rare earths present in phosphogypsum can be recovered by leaching the phosphogypsum at ambient temperature with a 0.1 to 0.5 M H_2SO_4 solution in a solid-to-liquid ratio of 1:10.[24] It is impossible to quantitatively recover the rare earths without destruction of the phosphogypsum lattice. The leaching efficiencies can be increased by a gravity flow of the H_2SO_4 solution through a column packed with phosphogypsum.[27] Another method for enhanced H_2SO_4 leaching is the mechanical activation of phosphogypsum by ball-milling.[28] The rare earths can be recovered from the leaching solution by precipitation, for instances as sodium rare-earth double sulphates,[29] or by solvent extraction.[24] Higher leaching efficiencies are obtained by

leaching with a HNO_3 solution instead of a H_2SO_4 solution.[30] Jarosinski and coworkers described a wasteless process for the recovery of rare earths from phosphogypsum (Figure 7).[31] The basic steps are: (1) leaching of the rare earths with dilute sulphuric acid from the phosphogypsum; (2) concentration of the leachate by evaporation, followed by recovery of the rare earths by solvent extraction with nonyl–phenyl phosphoric acid (NPPA) or by selective precipitation with hydrofluoric acid; (3) production of anhydrite (anhydrous calcium sulphate) from the purified phosphogypsum by recrystallisation in concentrated sulphuric acid. Different process parameters had to be used, depending on whether the starting materials were calcium sulphate hemihydrate or dihydrate. The purified anhydrite can be used for production of plaster. Not all rare earths present in phosphate rock end up in phosphogypsum. The process was tested on a pilot scale, but it is too complicated and uneconomical to be industrialised.

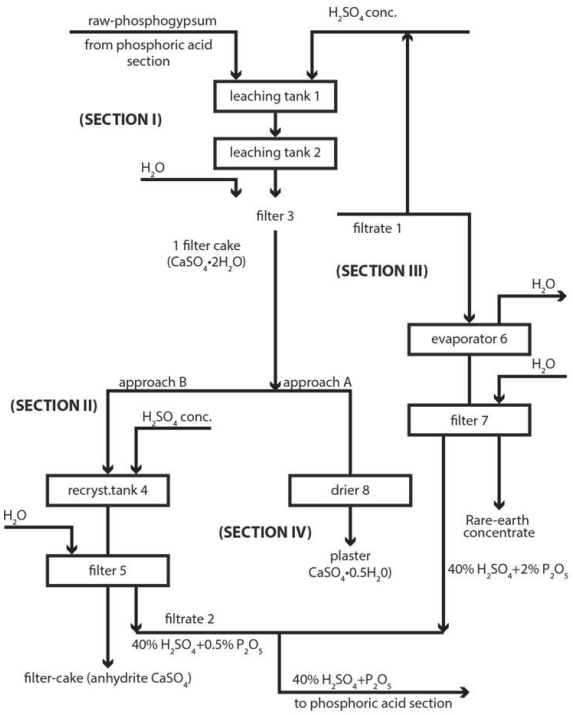

Figure 7: Process flow sheet for recovery of rare earths from phosphogypsum, with production of purified anhydrite for use as plaster. Adapted with ref. 31. Copyright Elsevier B.V.

Phosphogypsum can be decomposed by reaction with ammonium carbonate, so that ammonium sulphate fertiliser and calcium carbonate are formed.[24] The rare earths report to $CaCO_3$ and can be recovered by dissolution of $CaCO_3$ in HNO_3, followed by removal of the rare earths by solvent extraction. Alternatively, $CaCO_3$ can be calcined

to CaO and calcium can be dissolved by leaching with an NH_4Cl solution. This results in a rare-earth rich residue. When phosphate rock is leached with a HNO_3 solution, all the rare earths are solubilised as nitrates.[24] The HNO_3 leaching is more favourable than H_2SO_4 leaching for the recovery of rare earths from phosphate rock, but H_2SO_4 leaching is preferred in industry because of economic reasons. It is evident that HNO_3 leaching does not produce phosphogypsum.

Iron-rich sludges from the zinc industry

Large volumes of iron-rich sludges are produced by the Roast-Leach-Electrowinning (RLE) process of the zinc industry. The starting material for the RLE process is a zinc sulphide concentrate, which is converted into an oxidic product (zinc calcine) by roasting. The main zinc compound in the concentrate is sphalerite (ZnS) and it is often accompanied by galenite (Pb_S) and pyrite (FeS_2). The zinc concentrate contains many other elements as impurities: Sn, Pb, Ag, Hg, Mn, In, Tl, Ga, Ge, Co, Ni, Cd, Si... Sphalerite itself contains varying concentrations of iron, up to 30%. The three major zinc compounds in zinc calcine are zinc oxide (ZnO), zinc ferrite ($ZnFe_2O_4$) and zinc sulphate ($ZnSO_4$). The leaching of zinc calcine is typically done in two steps, a first step (neutral leaching) with a dilute H_2SO_4 solution to dissolve zinc oxide and zinc sulphate, and a second step (hot acid leaching) at high temperatures and high acid concentrations to dissolve the zinc ferrite. The second step brings iron into solution and this iron has to be removed from the zinc sulphate leaching solutions by precipitation. Iron(III) hydroxide forms gelatinous precipitates that are difficult to settle and filter, so that much research has been done to obtain readily filterable precipitates. The two major industrial processes for removal of iron by precipitation are the "jarosite process" and the "goethite process", both producing iron-rich sludges.[32,33]

In the "*jarosite process*", iron is precipitated as a complex basic iron(III) sulphate, $M(SO_4)_2Fe_3(OH)_6$ (M = Na, NH_4), from the hot acid leaching solution at elevated temperatures by addition of ammonium or sodium salts. The precipitation reaction releases acids, which must be neutralised. This is typically done by addition of zinc calcine. Different variations of the jarosite process have been developed, e.g. the "Outukumpu conversion process".

In the "*goethite process*", iron is precipitated from the zinc sulphate solution as goethite (α-FeOOH). The goethite process involves several steps: (1) reduction of iron(III) to iron(II) in the acidic leach solution by reaction with zinc sulphide concentrate; (2) filtration of the pulp; (3) preneutralisation of the filtrate with zinc calcine to a pH of about 2; (4) oxidation of iron(II) with air or oxygen back to iron(III), while maintaining the pulp at a pH close to 2 with stepswise addition of zinc calcine. A readiliy filterable goethite precipitate is formed, which is filtered off. The goethite

sludge is stored in tailing ponds for settling and dewatering, similar to the red mud tailing ponds, and the dry material is landfilled in monodeposits. In a modification of the process, the goethite slugde is dewatered by using a filter press, instead of pumping it into a tailing pond for settling and dewatering. The goethite process has been developed in Belgium by the Société de la Vieille Montagne (Union Minière, now Nyrstar).[34] In Europe, goethite landfills are found in Belgium, France, The Netherlands, Finland, Germany, Spain, Italy and Bulgaria. They are associated with the large zinc smelters in Europe from companies such as Nyrstar, Boliden, Glencore and KCM. About 10,000 ktonne of goethite stocks are stored in these landfills, while an annual *flow* of 500 ktonne fresh goethite is generated by the zinc industry.

The goethite process produces a residue that is somewhat richer in iron, between 30 and 40%, compared to an iron content between 28 and 32% for the jarosite process. The zinc recovery rate of this process is lower than the one obtained with the jarosite process. While the usual final zinc content found in the residue of the jarosite process is typical 3 to 4% of zinc, the final residue resulting from the goethite process contains up to 8 to 10% of zinc. On the other hand, the goethite process produces less waste (0.25 tonne of goethite for processing of 1 tonne of zinc concentrate) than the jarosite process (0.4 tonne of jarosite for processing of 1 tonne of zinc concentrate). It must be mentioned that besides goethite and jarosite, the Roast-Leach-Electrowinning (RLE) process produces also another solid zinc residue, resulting from the fraction of the zinc calcine that cannot be dissolved in acids during the leaching steps. This solid residue is landfilled, just as goethite and jarosite.

The iron-rich sludges from the zinc industry (jarosite and goethite) contain considerable amounts of critical elements, mainly indium, germanium, gallium and antimony. For instance, stockpiled goethite contains up to 500 g/tonne of indium (= 500 ppm) and 180 g/tonne of germanium (= 180 ppm). In contrast to bauxite residue and phosphogypsum, virtually no work has been done yet on the recovery of critical metals from these sludges. This is virtually uncharted territory that awaits further studies. Hardly any information is available on the concentrations of the minor elements in these iron-rich sludges, neither is there information on the distribution of these elements among different mineralogical phases. Researchers could be inspired by the hydrometallurgical and pyrometallurgical processes that have been developed for the recovery of metals from bauxite residue, because both goethite and bauxite residue are iron-rich. However, goethite is an acidic residue, while bauxite residue is alkaline. This means that in the case of acidic leaching of goethite residue no acid is consumed for neutralisation of an alkaline residue, in contrast to acid leaching of bauxite residue. On the other hand, goethite contains significant concentrations of lead, zinc and sulphur, whereas bauxite residue does not. Umicore has developed a pyrometallurgical process to recover indium and germanium from goethite by smelting the residues in a furnace comprising a submerged plasma torch generating an oxidising

gas mixture, and by feeding a solid reducing agent (e.g. coal, cokes) to the melt.[35] No special preparation of the goethite is required; wet goethite sludge can be used as feed. Indium and germanium are fumed together with zinc. These elements can be recovered from the flue dust and further processed. For instance, this process allows and upconcentration of indium from 400 ppm in goethite to 1350 ppm in the flue dust. For the recovery of metals from jarosite, research can find inspiration in the hydrometallurgical processes developed for the recovery of metals from phosphogypsum, since both jarosite and phosphogypsum are sulphates. However, jarosite is iron-rich, whereas phosphogypsum is not.

Goethite offers possibilities for further treatment, such as smelting or slag fuming to reduce the residual lead, zinc and sulphur content, and to obtain an inert material that can be used in the construction industry or as a starting material for the production of glass ceramics. In the 1990s Union Minière (Belgium) has developed a process for the inertisation and solidification of goethite.[36] The product (Graveliet®) can be used as a secondary construction material, as replacement for gravel in concrete or in the form of bricks. This process consists of mixing goethite with basic slag from the steel industry (blast furnace slag or converter slag). Basic slag contains an excess of free and reactive CaO. During mixing and further curing pozzolanic reactions take place between the acidic goethite and the basic slag and the product cures into a hard and inert solid material. Pilot-scale tests have been carried out in 1998, but the process has never been commercialised for various reasons. As part of a zero-valorisation approach, the transformation of goethite into a construction material could be combined with recovery of the critical metals.

Metallurgical slags

Efficient pyrometallurgical processes have been developed for the recovery of metal values from electronic scrap, spent automobile exhaust catalysts and spent industrial catalysts. In its Hoboken site near Antwerp (Belgium) Umicore operates an integrated smelter and refining plant for recovering metals from Waste Electrical and Electronic Equipment (WEEE).[37,38] Recovered metals include: silver, gold, indium, bismuth, tin, selenium, tellurium, antimony, arsenic, the platinum-group metals (platinum, palladium, ruthenium, rhodium, iridium) and the base metals copper, nickel and lead. However, the employed metallurgical flow sheets have not been developed for the recovery of rare earths. Due to the high affinity of the rare-earth metals for oxygen, these elements end up in diluted (oxidic) form in the slag of the so-called “copper smelter” and finally in the slag of the lead blast furnace. Moreover, the rare-earth content of these slags consists largely of cerium, which is not a critical metal. In fact, there is an oversupply of cerium, due to the large natural abundance of cerium and its relatively low demand.[39] Other companies such as Aurubis and Boliden use pyrometallurgical processes comparable to that of Umicore for the multi-metal

recycling from electronic scrap, but none of cases the rare earths are recovered from the slag phases.

Concurrently, pyrometallurgical flow sheets for the recycling of valuable metals from batteries can produce a slag relatively rich in rare earths. In 2011, Rhodia (Solvay) and Umicore announced that they had jointly developed a process for recycling of rare earths from nickel metal hydride rechargeable batteries.[40] Although the details of the process have not been disclosed, it is based on Umicore's patented Ultra High Temperature (UHT) smelting technology.[41] An industrial-scale pilot plant is operational in Hoboken since September 2011 and this pilot plant has an initial annual capacity of 7000 tonnes, corresponding to approximately 150000 (hybrid) electric vehicle batteries or 250 million mobile phone batteries. Not only nickel metal hydride batteries, but also lithium-ion batteries could be recycled in this facility. At this moment, the process has been optimised for End-of-Life portable nickel metal hydride batteries. The batteries are fed in a vertical shaft furnace, together with a small amount of coke and a slag former. At the bottom of the shaft furnace, oxygen-enriched air is injected into the furnace. The process requires relatively little external energy input, because the combustion of both the plastic casing of the batteries and the organic electrolytes releases large amounts of energy. The metals are converted into a Ni-Co-Cu-Fe alloy and a slag. The slag consists mainly of oxides of calcium, aluminium, silicon, and iron, and also contains lithium and rare earths.[42] These oxide slags can be processed to recover lithium and to produce rare-earth concentrates that are subsequently used as a feed in the rare-earth separation plant of Solvay (formerly Rhodia) in La Rochelle, France.

In comparison to natural ores, slags have the advantage that the formation of mineral phases during cooling can be influenced by use of different slag formers, cooling rates and furnace conditions. This processing of slags is defined as hot stage slag engineering.[43] The slag composition and microstructure can be changed by adjusting the primary pyrometallurgical process directly or immediately after separation of the slag from the molten metal, while the slag is still at high temperature. If a metal can be enriched in a certain mineralogical slag phase embedded in a matrix of other minerals by choosing a suitable slag composition and cooling trajectory, then a separation of this mineral phase might be possible by conventional ore processing methods. The metal could be much more effectively extracted from the resulting mineral concentrate than by processing the complete slag.[44] For instance, the affinity of neodymium and dysprosium to phosphate-containing phases was investigated for the Al_2O_3–CaO–MgO–P_2O_5–SiO_2 slag system, with slags originating from pyrometallurgical recycling of NdFeB magnets.[44] In the phosphate-free Al_2O_3–CaO–MgO–SiO_2 slag system, dysprosium and neodymium were more or less randomly distributed throughout the different silicate phases, although local enrichments of up to 15 wt% of rare-earth oxides were found. Addition of P_2O_5 led to the formation of a britholite-like

silicophosphate, with up to 57 wt% of rare-earth oxides. This phase formed at an early stage of the cooling process and it is assumed that it scavenged the rare earths before the silicate phases were crystallising.

Bottom ashes and fly from incineration plants

Municipal solid waste incineration (MSWI) is a vital part of many waste management systems. The residues formed during the incineration contain many valuable elements and have been investigated as secondary source of ferrous and non-ferrous metals. In a MSWI plant, the waste is incinerated at a temperature of 850–1000 °C, forming a solid bottom ash fraction and flue gas, which is captured and cooled to form boiler ash, fly ash and air pollution control (ACP) residues. A schematic overview of a MSWI plant is shown in Figure 8.[45] The waste incineration residues can undergo different treatments (e.g. dry, wet, thermal, mechanical) aimed at removing ferrous and non-ferrous metals and/or valorising it as a granulate for the construction industry, e.g. in road foundation. Many different elements are present in these ashes, reflecting the complex composition of municipal solid waste. The most common components are the oxides SiO_2, Al_2O_3, CaO, Fe_2O_3, Na_2O and K_2O.[46] The bottom ashes from municipal solid waste incineration plants could be a secondary source of chromium, copper, nickel, zinc and lead.[46] A study of the ashes of a Swiss incineration plant burning municipal solid waste showed that the concentrations of rare earths are very low and the extraction of these elements from the ashes would not be economically feasible.[47] Analysis of the metal content of a Danish and an Italian incineration plant gave similar low concentrations of rare earths.[48,49] The concentration of rare earths in Chinese medical waste incinerator ashes is lower than the crustal abundance of the rare earths.[50]

Fly ashes of incineration plants could be an interesting secondary resource for antimony. 70 % of today´s worldwide antimony consumption is in the form of Sb_2O_3 as flame retardant in plastic products. A major part of these antimony compounds is bound in the plastic fraction of WEEE scrap such as TV and computer casings or printed circuit boards. Most of antimony content from these end-of-life products ends up in incineration plants, where different wastes (including the plastic fraction from WEEE) are burnt. The volatile Sb_2O_3 is carried out via off-gas and is collected in flue dusts (fly ashes). Typical antimony contents in such dusts can vary between 260 and 1100 ppm depending on the feedstock and treatment parameters.[51] However, presorting of materials with high antimony contents (e.g. plastics with flame retardants), could drastically improve the efficiency of such an incineration process, leading to fly ashes with a much higher antimony content.

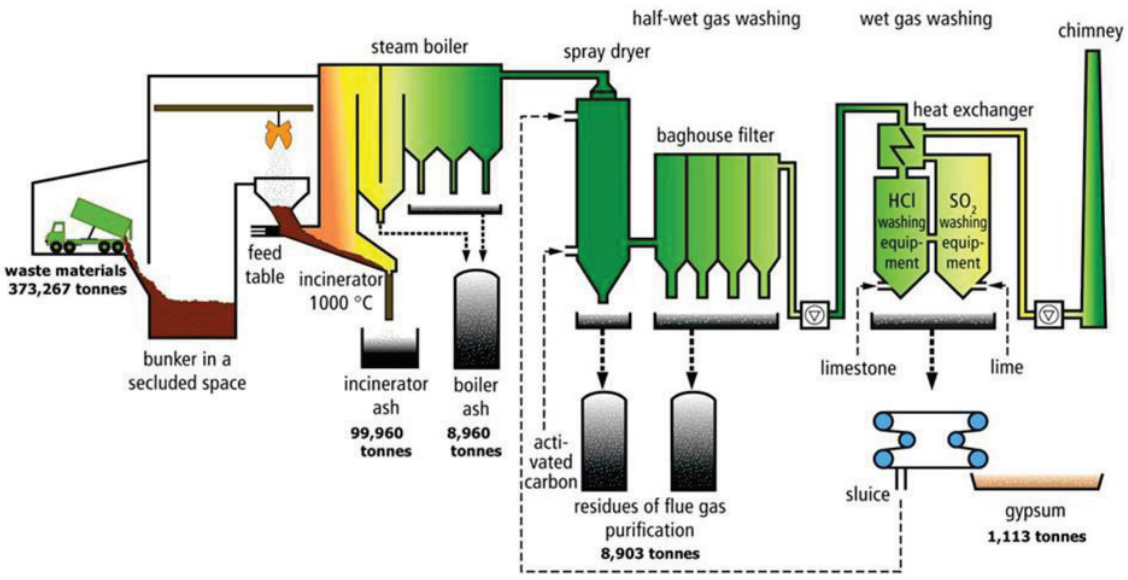

Figure 8: Schematic representation of the MSWI plant in Doel, Belgium. Figure reproduced from ref. 45. Copyright: KU Leuven

Towards zero-waste valorisation of industrial process residues

In this paper we have used the term "valorisation" to refer to the economically viable utilisation of a material stream which was hitherto considered as a non-valuable waste stream. The term "valorisation" differs from the official meaning of the word in UK English where it is described as the increase in the value of capital assets through the application of value-forming labour in production. However, as the term "valorisation" has been used for many years by a multitude researchers in the context of "slag valorisation"[52] or "waste valorisation", we also employ it in this meaning in the present review paper. Hence, valorisation of landfilled *stock*s and *flow*s of industrial process residues implies that a certain value is created in a cost-effective way.

When considering the valorisation of critical-containing secondary resources, one can take a straightforward metal-centric approach in which the only critical metals are extracted from the residue. As these metals form only a minor fraction of the overall residue, the chosen metal-centric processing method is only delivering a suboptimal solution, in which the largest fraction of the residue is not catered for, often implying that more costly and environmentally-unfavourable stockpiling or landfilling is required. It is clear that this metal-centric approach is not in line with the whole-system approach that is conveyed by the zero-waste philosophy. The latter strives to eliminate waste at source and at all points down the supply chain, thereby rejecting one-way linear resource-use in favour of a "closed-loop" circular system.[53] Translated

to the domain of zero-waste valorisation of landfilled *stock*s and *flows* of metal-containing industrial process residues, this implies that a metal-centric recovery approach needs to be replaced by a product-centric, whole system approach, in which (almost) all components of the residue need to be turned into value, i.e. "valorised". The rejection of a metal-centric in favour of a product-centric approach has received ample attention in the most recent UNEP report Metal Recycling – Opportunities, Limits, Infrastructure.[54] Although the concept was mainly developed for the integrated valorisation of critical and technology metal containing End-of-Life products (cf. Waste Electrical and Electronic Waste, WEEE), it is perfectly fit for secondary resources as well. In the context of End-of-Life products, it has been pointed out that the product-centric view considers the complex metallurgy of all elements at the same time, optimising both the metallurgy and recycling infrastructure in order to minimise losses, but also addressing the related issues, such as liberation, sorting and consumer recycling.[55]

The work of Reuter and colleagues demonstrates that zero-waste valorisation will require more than the development of technological solutions, as also pointed out by Klauber et al..[56] In the case of industrial process residues, the "secondary resource" should thus be regarded as a polymetallic raw material product, also hosting a number of potentially valuable minerals. Zero-waste, product-centric valorisation, therefore, means that tailored, integrated flow sheets need to be designed to recover both critical and base metals, while simultaneously finding solutions for the residual mineral matrix as well. For instance, in the case of stocks of previously produced bauxite residue, this zero-waste vision implies that all valuable metals (including the lanthanides and scandium) etc. need to be recovered, while valorising the mineral matrices into, for example, innovative construction materials (e.g. alternative binders that can replace Portland Cement). An even more ideal, whole-system scenario is to redesign the overall flow sheet upstream so that different residues are generated, which can find better valorisation options further downstream the valorisation chain.

For instance, zero-waste valorisation of bauxite residue implies not only removal of the rare earths and other metal values, but also finding applications for the metal-lean residues. The removal of rare earths can be done in a preprocessing step consisting of leaching the rare earths from bauxite residue, followed by further processing of the remaining residue for recovery of the other metals. However, other processing schemes are possible. For instance, the rare earths could be removed from the slag that are formed during the removal of iron as pig iron. An example is the ENEXAL bauxite residue treatment process, developed by Aluminium of Greece, and demonstrated on pilot-plant scale.[57,58] Through electric arc furnace carbothermic smelting, bauxite residue is fully converted into two marketable products: pig iron and mineral wool. Pig iron is used in the secondary steel industry as a steel scrap substitute, while the mineral wool can applied for the production of thermo-acoustic

insulating products for the construction industry. No solid or liquid waste products are generated in this process, and thus in conjunction with the alumina refinery plant, zero-waste valorisation of the bauxite ore can be achieved. So recovery of rare earths is not done in the ENEXAL process, but new process flow sheets with recovery of rare earths could be developed.

Conclusions and outlook

Previously landfilled *stocks* and freshly produced *flows* of the solid industrial process residues from the metallurgical, phosphate and incineration industry often contain significant concentrations of critical metals (e.g. rare earths, indium, germanium and antimony). However, the recovery of metals from these secondary residues is a major challenge. The extractive metallurgy of metal-containing, industrial process residues is complex because these often contain a large number of metals in small concentrations, and often locked in complex sulphides, oxides, phosphates or silicates. Consequently, it is difficult to dissolve the metals in either strong acids or alkalis. The hydrometallurgical methods often lack selectivity: the valuable metals, but also unwanted metals, are co-dissolved.

Therefore, new sustainable metallurgical methods have to be developed for processing these residues. A product-centric approach, rather than a metal-centric approach has to be targeted in the sense that the secondary residue is a by-product which needs a zero-waste solution, implying the recovery of the base, technology and critical metals, while also taking care of the residual mineral matrix that is left behind in the case of solid residues. The developed solutions are relevant for both (landfilled) *stocks* and (freshly produced) *flows* of these residues. As regards these *stocks*, the Enhanced Landfill Mining definition, which was primarily developed for Urban Solid Waste landfills, can be extended to mono-landfills containing industrial process residues. Considering that Europe has a large amount of these landfills associated with its rich industrial ecosystem, the developed zero-waste flow sheets can provide the EU with an independent source of both critical and economically important metals, while simultaneously delivering ample quantities of minerals for low-carbon engineered products (e.g. building materials). As these mono-landfills are typically owned by the industries producing these residues, ELFM is more straightforward for these – typically large and homogeneous –deposits than for the more complex, often smaller, and typically publicly owned Urban Solid Waste landfills.

Nevertheless, a lot of research is still to be done to develop economic, zero-waste flow sheets for these industrial process residues. Although the metal prices will largely determine the overall business case, the economics can be improved by developing zero-waste flow sheets in which higher added value applications for the mineral

matrices can be delivered. As prioritised by the European Commission in its new Action Plan for the Circular Economy, major R&D efforts are required in this domain.

Acknowledgments

The authors wish to acknowledge KU Leuven for financial support (projects GOA/13/008 and IOF-KP RARE^3).

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